ABSTRACT

Interfacial strength between polymeric matrix and lignocellulosic reinforcement has direct effects on the properties of wood plastic composites (WPCs). There are two approaches to improve the interfacial adhesion between two phases in WPC: modification of the polymeric matrix or modification of the lignocellulosic fibres. This work focuses on the chemical modifications of natural fibres such as lignocellulosic, enhanced by silane, alkali, benzoyl chloride and acid acrylic. The chemically treated fibres were then compounded with polypropylene at 190°C and 40 wt%, in an internal mixer equipped with cam rotor, for all samples. Changes in the chemical structure of chemically treated fibres were tracked by Fourier transform infra red (FTIR) spectroscopy. The intensity of O-H bond at 3400 cm⁻¹ and formation of ester bond at 1740 cm⁻¹ were indications of changes in the chemical structure of the fibres. The interfacial adhesion was evaluated using adhesion factor which was obtained from dynamic mechanical thermal analysis data. The results showed that the minimum adhesion factor is related to silane treatment which provides the best interaction between polymer and fibres. The tan δ peak was shifted to higher temperature for filled samples in comparison to neat polypropylene and the amount of shift was related to the method of chemical treatment. Different morphologies were observed in samples due to different chemical modifications of fibres and among them, silane treatment method of the fibres provides the best wetting action by polymeric matrix. Tensile properties and impact resistance of the samples were determined to evaluate the effect of interfacial adhesion on the performance of the composites.

INTRODUCTION

Wood-polymer composites (WPC) have gained world interest in recent years. Applications for these composites include construction, industrial and automotive products. Wood and natural polymer composites are environmentally biodegradable, less abrasive on processing equipments, and lighter in weight compared to mineral-filled composites.

Strength of interfacial phase is an important criterion in properties of WPCs. Due to polarity mismatching of natural fibres and plastics, their interfacial boundaries are often weak and lead to undesirable mechanical properties. Many studies have been carried out to improve the adhesion between two phases including incorporation of coupling agent into the
compound and modification of the fibres.

Different coupling agents have been used to modify the polymeric matrix and improve the interfacial strength and subsequently the mechanical properties of the products. Maleic anhydride grafted styrene-ethylene-butylene-styrene (SEBS-g-MA) [1] and maleic anhydride grafted polyolefin (HDPE-g-MA, PP-g-MA, and LDPE-g-MA) [2-5] are the most common examples of reported works in the literature.

Another approach for enhancement of interfacial adhesion in WPC is fibre treatment before mixing with polymer. Some of these treatments have physical nature and some of them are of chemical nature. Plasma and corona treatments of the fibres (as physical methods) have been reported by Gassan et al. [6] and Yuan et al. [7]. Their results show enhanced polymer-matrix adhesion.

Natural fibres have a good potential for chemical treatment due to presence of hydroxyl groups in lignin and cellulose. Reaction of hydroxyl groups can change the surface energy and the polarity of the natural fibres. Many studies have been undertaken to modify the performance of natural fibres. Different surface treatment methods such as mercerization (alkali treatment) [8-10], isocyanate treatment [11,12], acrylation [13,14], benzoylation [14,15], latex coating [16], permanganate treatment [17], acetylation [18], silane treatment [19-23] and peroxide treatment [24] have been applied on the fibre to improve its strength, size and its shape and the fibre-matrix adhesion. The aforementioned methods have their own merits and demerits, e.g., alkali treatment improves the fibre-polymer adhesion due to the removal of natural and artificial impurities and changes in chemical composition of the fibre by removing the cementing substances like lignin and hemicelluloses [25].

Mechanisms of the performance of these methods are different and depend on the chemical structure of the reagents. For example, Sreekala et al. [26] have reported that the peroxide-induced grafting of polyethylene onto cellulose surfaces is formed by reaction of peroxide radicals, produced by decomposition of peroxide, with cellulose.

The aim of this study was to investigate of influence of wood fibre surface treatment on the interfacial strength of polypropylene/wood flour composites. Chemical modifications of the natural fibres were completed using silane, hydroxide sodium, benzoyl chloride and acrylic acid. The effects of chemical treatments on the interfacial behaviour were evaluated by dynamic mechanical analysis (adhesion factor), mechanical properties (tensile and impact) and morphology studies.

EXPERIMENTAL

Materials
Polypropylene was purchased from Arak Petrochemical Co., Iran (trade name: V30s, MFI = 16 g/10 min, and density 0.9 g/cm³). Polypropylene-g-maleic anhydride (MAPP) as coupling agent was purchased from Solvay Co., Belgium (MFI = 64 g/10 min and contains 0.1% maleic anhydride).

Beech fibres were prepared from local market in Sari, Iran. The characteristics of the natural fibres (aspect ratio distribution and chemical composition) are shown in Figure 1. The chemical structure of natural fibres was measured according to TAPPI standard and aspect ratio was obtained using optical microscopy. tri-Ethoxy vinyl silane, acrylic acid, benzoyl chloride and sodium hydroxide were purchased from Merck, Germany.

Fibre Treatment
Treatment with Sodium Hydroxide
The wood fibres were immersed in 2% solution of NaOH for half an hour and then washed with distilled
water containing a few percent of acetic acid to remove the alkali residue. Washing was continued to remove all traces of alkali. The washed fibres were then dried in an oven at 80°C for 24 h. The proposed reaction for this treatment is given in the following equation [9]:

$$\text{Fibre} - \text{OH} + \text{NaOH} \rightarrow \text{Fibre} - \text{O}^- \text{Na}^+ + \text{H}_2\text{O}$$

The main reaction is between OH groups of cellulose and the hydrogen of the alkali.

**Treatment with Benzoyl Chloride**

The fibres (products of alkali treatment) were dipped in solution of 5% of NaOH and benzoyl chloride for 15 min. Ethanol solution was used to remove the excess benzoyl chloride for another hour. Finally, the fibres were washed with distilled water and dried in oven at 80°C for 24 h. The reactions in this treatment can be illustrated as follows [13]:

$$\text{Fibre} - \text{OH} + \text{NaOH} \rightarrow \text{Fibre} - \text{O}^- \text{Na}^+ + \text{H}_2\text{O}$$

![Chemical structure of benzoyl chloride reaction](image)

**Treatment with Acrylic Acid**

The fibres (the products of alkali treatment) were immersed in acrylic acid solution at 50°C for half an hour and then washed and dried as previous treatments. The reaction was accomplished between OH groups and acrylic acid [14] as follows:

$$\text{Fibre} - \text{OH} + \text{CH}_2 = \text{CH} - \text{COOH} \rightarrow$$

$$\text{Fibre} - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{COOH}$$

**Treatments with Silane**

The NaOH treated wood fibres were immersed into a mixture of ethanol/water (60/40 ratio) for 2 h. The pH of the solution was kept between 3.5 and 4 by adding pure acetic acid. The washing and drying steps were repeated as in previous treatments. The possible chemical reactions are as the following steps [20]:

$$\text{CH}_2 = \text{CH} - \text{Si}(\text{OC}_2\text{H}_5)_3 \rightarrow \text{CH}_2 = \text{CH} - \text{Si(OH)}_3$$

$$\text{Fibre} - \text{OH} + \text{CH}_2 = \text{CH} - \text{Si(OH)}_3 \rightarrow$$

$$\text{Fibre} - \text{O} - \text{Si(OH)}_2 \text{CH} = \text{CH}_2$$

The modified fibres were characterized by FTIR spectroscopy.

**Sample Preparation**

Polypropylene and modified fibres were weighed and bagged. Natural fibre content was constant (40 wt%) in all samples. They were then blended at 190°C for 8 min at 60 rpm using a Haake internal mixer equipped with a cam rotor type (SYS 9000, USA). The fibres were added to mixing chamber after two minutes of melting PP. The compounded materials were then ground to prepare the granules using a pilot scale grinder (Wiesler, WGLS 200/200 model, Germany). The resulted granules were dried at 105°C and were stored under controlled conditions (50% relative humidity and 23°C) for at least 40 h prior to testing.

**Measurements**

Dynamic mechanical analysis (DMTA) was accomplished by Triton, Model Tritic 2000, UK. The dimension of each sample was 5×1×2 cm. The range of testing temperature was from -50 to 150°C and the experiments were carried out at 1 Hz frequency. The experiment was performed in the triple-point bending mode.

Tensile properties were determined according to ASTM D-638 by Instron 6025 model, UK. Izod impact strength test was carried out according to ASTM D-256 using, Zwick 5102 model machine, Germany. To study the microstructure of composites, scanning electron microscopy (Jeol jxa-840, Japan) was performed on cryogenically fractured surface.
RESULTS AND DISCUSSION

Figure 2 exhibits the FTIR spectra of treated and untreated wood samples. As can be seen the O-H bond at 3400 cm\(^{-1}\) is affected by alkali treatment and its intensity is decreased (Figure 2d). The main reason for this behaviour is that by NaOH treatment an amorphous region is developed in cellulose by removal of OH groups from its network. In other words, the surface of alkali treated sample is accomplished with more available O-H groups.

The intensity of the bond at 1740 cm\(^{-1}\) is increased due to formation of ester bonds from the reaction between O-H groups and benzoyl chloride (Figure 2b), while the O-H band intensity tends to decrease due to its consumption in this reaction.

The effect of wood fibre modification on the interfacial strength was tracked using adhesion factor. This parameter is obtained from DMTA data which has been originated from Kubat et al. work on high density polyethylene filled with 20 vol\% glass fibre [27]. These researchers assumed that the mechanical loss factor (\(\tan \delta_c\)) of the composite can be given as follows:

\[
\tan \delta_c = V_f \tan \delta_f + V_i \tan \delta_i + V_m \tan \delta_m \tag{1}
\]

where, the \(f\), \(i\), and \(m\) subscripts denote filler, interphase, and matrix, and \(V\) is the volume fraction. By considering \(\delta_f \approx 0\) and since the volume fraction of the interphase is rather small, eqn (1) can be rearranged as follows:

\[
\frac{\tan \delta_c}{\tan \delta_m} \approx (1 - V_f)(1 + A) \tag{2}
\]

\[
A = \frac{V_i}{1 - V_f} \frac{\tan \delta_i}{\tan \delta_m} \tag{3}
\]

where, eqn (3) can be rewritten as given in eqn (4):

\[
A = \frac{1}{1 - V_f} \frac{\tan \delta_i}{\tan \delta_m} - 1 \tag{4}
\]

By calculating adhesion factor from DMTA data, one can interpret the strong interactions between the wood fibres and polymer matrix of the interphase due to reduction of macromolecular mobility in the vicinity of filler surface which leads to lower adhesion factor. In other words, a low value of adhesion factor is an indication of good adhesion or high degree of interaction between the two phases [28].

The adhesion factor versus temperature is illustrated in Figure 3 as an evaluation parameter for lignocellulosic filler-polymer interactions. This factor presents a macroscopic quantitative measure of interfacial adhesion during dynamic loading. As can be seen, below glass transition temperature, the maximum amount of adhesion factor is related to untreated samples, which means that the weakest interface is formed for samples containing untreated lignocellulosic fillers. It seems that, the silane
treatment facilitates the interaction between filler-polymer and lowers the adhesion factor. The probable mechanism can be proposed as follows: first, the silanol groups are formed by moisture hydrolyzation. These groups are able to react with cellulose, hemicellulose and lignin of lignocellulosic fillers and form strong covalent bonds. At the same time, the other end of silane has olefinic structure and is miscible with polypropylene and results in stronger interaction between the phases. Similar mechanism for different silane coupling agents is proposed by Jaya et al. [21]. It is important to note that adhesion factor seems to be very sensitive to glass transition temperature of the samples. Around this temperature, the adhesion factor reaches its maximum value due to higher mobility of polymer chains. In other words, a strong interfacial adhesion (i.e., samples which are treated with silane) restricts the chain mobility at the filler-matrix interface, therefore the adhesion factor decreases and its maximum point shifts to higher temperature.

Figure 4 shows the variation of tan δ versus temperature for all samples. The tan δ peak is shifted to higher temperature for filled samples in comparison to neat polypropylene. Table 1 depicts the shift in glass transition temperature of the samples which is deduced from tan δ curves. Depending on the nature of lignocellulosic filler and filler/matrix interaction, glass transition of the composites shifts to higher temperatures. In other words, during stress transfer at the interface, the strong bonding causes the fibre constraint and the poor bonding leads to dissipation of energy. The maximum shift in peaks of tan δ is observed for samples containing silane treated wood fibres. This is an indication of more developed fibre/matrix interactions.

SEM Micrographs of samples with different treatments are demonstrated in Figure 5. As it may be seen, the sample without chemical treatment of its wood fibres is pulled out easily and some holes are noticed around the fibres which imply that there are weak interactions between the filler and polymer. The breaking mode of wood fibres has been changed with chemical treatment and breakage of both wood fibres and matrix occur simultaneously.

In samples undergone alkali treatment, the pull out of the wood fibres are still observed in some regions which means that the interactions between the phases are not strong enough. Similar trend is also observed for samples containing benzoyl treated fibres. The best encapsulation of wood fibres with polymer matrix can be seen in samples with silane treatment.

It is well known that, dispersion of reinforcing agent and interfacial adhesion between the two phases are the most determining parameters in mechanical properties of the composites. In this study, to evaluate the efficiency of chemical treatment of wood fibres, the mechanical properties were examined. Figure 6 shows the impact resistance of samples. Due to formation of stress concentration sites by lignocellulosic materials in the PP matrix and its rigid nature, it is expected that incorporation of wood fibre into PP causes dramatic depreciation of this property [29]. However by applying chemical treatment, the hydrophilic nature of lignocellulosic fillers are reduced for better dispersion of the filler into the polymer matrix. This phenomenon leads to

![Figure 4. Plots of tan δ vs. temperature for samples.](image-url)

Table 1. Shift in glass transition temperature of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shift in Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Unmodified</td>
<td>2</td>
</tr>
<tr>
<td>Acrylation</td>
<td>7</td>
</tr>
<tr>
<td>Benzoylation</td>
<td>8</td>
</tr>
<tr>
<td>Alkaline</td>
<td>6</td>
</tr>
<tr>
<td>Silane</td>
<td>13</td>
</tr>
</tbody>
</table>

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**Table 1.** Shift in glass transition temperature of the samples.
higher impact resistance in comparison to samples containing untreated filler.

Tensile strength and modulus of the samples are demonstrated in Figure 7. In general, PP/wood fibre composites show higher modulus and tensile strength compared to pure PP. The effect of surface treatment of wood fibre on the tensile properties of the composite is more apparent. A good dispersion of the fibres in the polymer matrix produces a uniform medium for transferring the stress and as a result the tensile strength is increased. In addition, reinforcement of the interfacial phases due to chemical treatment is the main reason for the enhancement of the modulus of the system in comparison with PP and those samples with unmodified fibres.
CONCLUSION

This research work presents an analysis of the interfacial behaviour of WPC composites based on polypropylene and beech wood fibres. Four chemical modification methods (silane, hydroxide sodium, benzoyl chloride and acid acrylic) were applied on wood fibres under study. The WPC samples were prepared by melt mixing in an internal mixer at 190°C and 40 wt% of wood fibres. The interfacial adhesion, morphology and the mechanical properties of the samples were studied and the concluding results are as follows.

- FTIR spectra of treated wood fibres show that the intensity of the bonds at 3400 and 1740 cm\(^{-1}\) change due to reaction of O-H groups and formation of ester groups in samples.
- The maximum amount of adhesion factors are related to untreated samples which means the weakest interface is formed for samples containing untreated lignocellulosic fillers. Chemical treatment facilitates the interactions between fillers-polymer and decreases the adhesion factor.
- The maximum shift in peak of tan $\delta$ has been observed for samples containing silane treated wood fibres due to highest interaction taking place between the fibres and polymer matrix.
- SEM Micrographs showed that the best encapsulation of wood flour by polymer matrix is observed in samples of silane treated fibres.
- Chemical treatment of lignocellulosic fillers results in better dispersion of the filler into the polymer matrix and leads to higher impact resistance in comparison with samples containing filler with no chemical treatment.

REFERENCES

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